

# Legacy and emerging perfluoroalkyl substances in the Cape Fear River Watershed of North Carolina: Occurrence and fate during conventional and advanced water treatment processes

Mei Sun<sup>1,2,\*</sup>, Elisa Arevalo<sup>2</sup>, Mark Strynar<sup>3</sup>, Andrew Lindstrom<sup>3</sup>, and Detlef R.U. Knappe<sup>2</sup>

**Supporting information includes analytical method description, 6 tables, and 5 figures.**

<sup>1</sup>Department of Civil and Environmental Engineering

University of North Carolina at Charlotte

Charlotte, North Carolina 28223, USA

<sup>2</sup> Department of Civil, Construction, and Environmental Engineering,

North Carolina State University, Campus Box 7908

Raleigh, North Carolina 28695, USA

<sup>3</sup> National Exposure Research Laboratory

U.S. Environmental Protection Agency

Research Triangle Park, North Carolina 27711, USA

**Analytical standards:** PFASs studied in this research are listed in Table S1. For legacy PFASs, native and isotopically labeled standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Native PFPrOPrA was purchased from Thermo Fisher Scientific (Waltham, MA). No analytical standards were available for other PFECAs.

**PFAS quantification:** PFAS concentrations in samples from DWTPs and adsorption tests were determined by liquid chromatography tandem mass spectrometry (LC-MS/MS) using a large-volume (0.9 mL) direct injection method. An Agilent 1100 Series LC pump and PE Sciex API 3000 LC-MS/MS system equipped with a 4.6 mm x 50 mm HPLC column (Kinetex C18 5 $\mu$ m 100 $\text{\AA}$ , Phenomenex Inc.) was used for PFAS analysis. The eluent gradient is shown in Table S4 in SI. All samples, calibration standards, and quality control samples were spiked with isotopically labeled internal standards, filtered through 0.45- $\mu$ m glass microfiber syringe filters, and analyzed in duplicate. The MS transitions for PFAS analytes and internal standards are shown in Table S5 in SI. The quantitation limit (QL) was 25 ng/L for PFOS and perfluorodecanoic acid, and 10 ng/L for other legacy PFASs and PFPrOPrA. For PFECAs without analytical standards, chromatographic peak areas are reported.

PFAS concentrations along the treatment train of DWTP C were analyzed using a Waters Acquity ultra performance liquid chromatograph interfaced with a Waters Quattro Premier XE triple quadrupole mass spectrometer (Waters, Milford, MA, USA) after solid phase extraction. Method details are described elsewhere.[ ADDIN EN.CITE

<EndNote><Cite><Author>Nakayama</Author><Year>2007</Year><RecNum>24</RecNum><DisplayText><style face="superscript">1</style></DisplayText><record><rec-number>24</rec-number><foreign-keys><key app="EN" db-id="rx5ets9t3v5ta9e2vz0xv2a2erzffpvrt ea" timestamp="1469820266">24</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Nakayama, Shoji</author><author>Strynar, Mark J.</author><author>Helfant, Laurence</author><author>Egeghy, Peter</author><author>Ye, Xibiao</author><author>Lindstrom, Andrew B.</author></authors></contributors><titles><title>Perfluorinated compounds in the Cape Fear drainage basin in North Carolina</title><secondary-title>Environmental Science & Environmental Engineering</secondary-title></titles></record></EndNote>

Technology</secondary-title></titles><periodical><full-title>Environmental Science & Technology</full-title></periodical><pages>5271-5276</pages><volume>41</volume><number>15</number><dates><year>2007</year><pub-dates><date>2007/08/01</date></pub-dates></dates><publisher>American Chemical Society</publisher><isbn>0013-936X</isbn><urls><related-urls><url><http://dx.doi.org/10.1021/es070792y></url></related-urls></urls><electronic-resource-num>10.1021/es070792y</electronic-resource-num></record></Cite></EndNote>] The QL for all PFASs with analytical standards was 0.2 ng/L, and peak areas were recorded for PFECAAs without standards.

Table S1. Perfluoroalkyl substances (PFASs) detected in the Cape Fear River (CFR) watershed

Compound	Molecular weight	Formula	CAS #	# of perfluorinated carbons	Chain length (including all C, O and S)
<b>Perfluorocarboxylic acids (PFCAs)</b>					
Perfluorobutanoic acid (PFBA)	214.0	C <sub>4</sub> HF <sub>7</sub> O <sub>2</sub>	375-22-4	3	4
Perfluoropentanoic acid (PFPeA)	264.0	C <sub>5</sub> HF <sub>9</sub> O <sub>2</sub>	2706-90-3	4	5
Perfluorohexanoic acid (PFHxA)	314.1	C <sub>6</sub> HF <sub>11</sub> O <sub>2</sub>	307-24-4	5	6
Perfluoroheptanoic acid (PFHpA)	364.1	C <sub>7</sub> HF <sub>13</sub> O <sub>2</sub>	375-85-9	6	7
Perfluorooctanoic acid (PFOA)	414.1	C <sub>8</sub> HF <sub>15</sub> O <sub>2</sub>	335-67-1	7	8
Perfluorononanoic acid (PFNA)	464.1	C <sub>9</sub> HF <sub>17</sub> O <sub>2</sub>	375-95-1	8	9
Perfluorodecanoic acid (PFDA)	514.1	C <sub>10</sub> HF <sub>19</sub> O <sub>2</sub>	335-76-2	9	10
<b>Perfluorosulfonic acids (PFSAs)</b>					
Perfluorobutane sulfonic acid (PFBS)	300.1	C <sub>4</sub> HF <sub>9</sub> SO <sub>3</sub>	29420-49-3	4	5
Perfluorohexane sulfonic acid (PFHxS)	438.2	C <sub>6</sub> HF <sub>13</sub> SO <sub>3</sub>	355-46-4	6	7
Perfluorooctane sulfonic acid (PFOS)	500.1	C <sub>8</sub> HF <sub>17</sub> SO <sub>3</sub>	111873-33-7	8	9
<b>Perfluoroalkyl ether carboxylic acids with one ether group (mono-ether PFECAs)</b>					
Perfluoro-2-methoxyacetic acid (PFMOAA)	180.0	C <sub>3</sub> HF <sub>5</sub> O <sub>3</sub>	674-13-5	2	4
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	230.0	C <sub>4</sub> HF <sub>7</sub> O <sub>3</sub>	377-73-1	3	5
Perfluoro-4-methoxybutanoic acid (PFMOBA)	280.0	C <sub>5</sub> HF <sub>9</sub> O <sub>3</sub>	863090-89-5	4	6
Perfluoro-2-propoxypropanoic acid (PFPrOPrA )	330.1	C <sub>6</sub> HF <sub>11</sub> O <sub>3</sub>	13252-13-6	5	7
<b>Perfluoroalkyl ether carboxylic acids with multiple ether group (multi-ether PFECAs)</b>					
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	246.0	C <sub>4</sub> HF <sub>7</sub> O <sub>4</sub>	39492-88-1	3	6
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	312.0	C <sub>5</sub> HF <sub>9</sub> O <sub>5</sub>	39492-89-2	4	8
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	378.1	C <sub>6</sub> HF <sub>11</sub> O <sub>6</sub>	39492-90-5	5	10

Table S2. Operational conditions of DWTP C on sampling day (August 18, 2014)

Parameter	Value
Raw water ozone dose	3.1 mg/L
Raw water total organic carbon concentration	6.0 mg/L
Aluminum sulfate coagulant dose	43 mg/L
Coagulation pH	5.70
Settled water ozone dose	1.3 mg/L
Settled water total organic carbon concentration	1.90 mg/L
Empty bed contact time in biological activated carbon filters	9.4 minutes for granular activated carbon layer 2.3 minutes for sand layer
Medium pressure UV dose	25 mJ/cm <sup>2</sup>
Free chlorine dose	1.26 mg/L as Cl <sub>2</sub>
Free chlorine contact time	17.2 hours

Table S3. Water quality characteristics of surface water used in adsorption tests

Non-purgeable organic carbon (mg/L)	Ultraviolet absorbance at a wavelength of 254 nm	pH	Alkalinity (mg/L as CaCO <sub>3</sub> )	Conductivity (μS/cm)
9.036	0.399	7.53	19	133.5

Table S4. LC gradient method for PFAS analysis

Time (min)	Mobile Phase A% (v/v)	Mobile Phase B%	Flow Rate (mL/min)
0 – 2	95	5	0.9
2 – 5	95	5	0.9
5 – 10	95 → 10	5 → 90	0.9
10 – 10.1	10	90	0.9
10.1 – 14	10 → 95	90 → 5	0.9

Mobile phase A: 2 mM ammonium acetate in ultrapure water with 5% methanol

Mobile phase B: 2 mM ammonium acetate in acetonitrile with 5% ultrapure water

Table S5. MS transitions for PFAS Analysis

	Compound	MS/MS Transition	Internal standard
Legacy PFASs	PFBA	212.8 → 168.8	13C4-PFBA
	PFPeA	262.9 → 218.8	13C2- PFHxA
	PFHxA	313.6 → 268.8	13C2- PFHxA
	PFHpA	362.9 → 318.8	13C4- PFOA
	PFOA	413.0 → 368.8	13C4- PFOA
	PFNA	463.0 → 418.8	13C4- PFOA
	PFDA	513.1 → 68.8	13C2-PFDA
	PFBS	299.1 → 98.8	18O2-PFHxS
	PFHxS	399.1 → 98.8	18O2-PFHxS
	PFOS	498.9 → 98.8	13C4-PFOS
PFECAAs	PFMOAA	180.0 → 85.0	N/A
	PFMOPrA	229.1 → 184.9	N/A
	PFMOBA	279.0 → 234.8	N/A
	PFPrOPrA	329.0 → 284.7	13C2- PFHxA
	PFO2HxA	245.1 → 85.0	N/A
	PFO3OA	311. → 84.9	N/A
	PFO4DA	377.1 → 85.0	N/A
Internal standards	Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]butanoic acid (13C4-PFBA)	217.0 → 172	Not applicable
	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]hexanoic acid (13C2-PFHxA)	315.1 → 269.8	
	Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>2</sub> ]octanoic acid (13C4-PFOA)	417.0 → 372.0	
	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]decanoic acid (13C2-PFDA)	515.1 → 469.8	
	Sodium perfluoro-1-hexane[ <sup>18</sup> O <sub>2</sub> ]sulfonate (18O2-PFHxS)	403.1 → 83.8	
	Sodium perfluoro-1-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octane sulfonate (13C4-PFOS)	502.9 → 79.9	

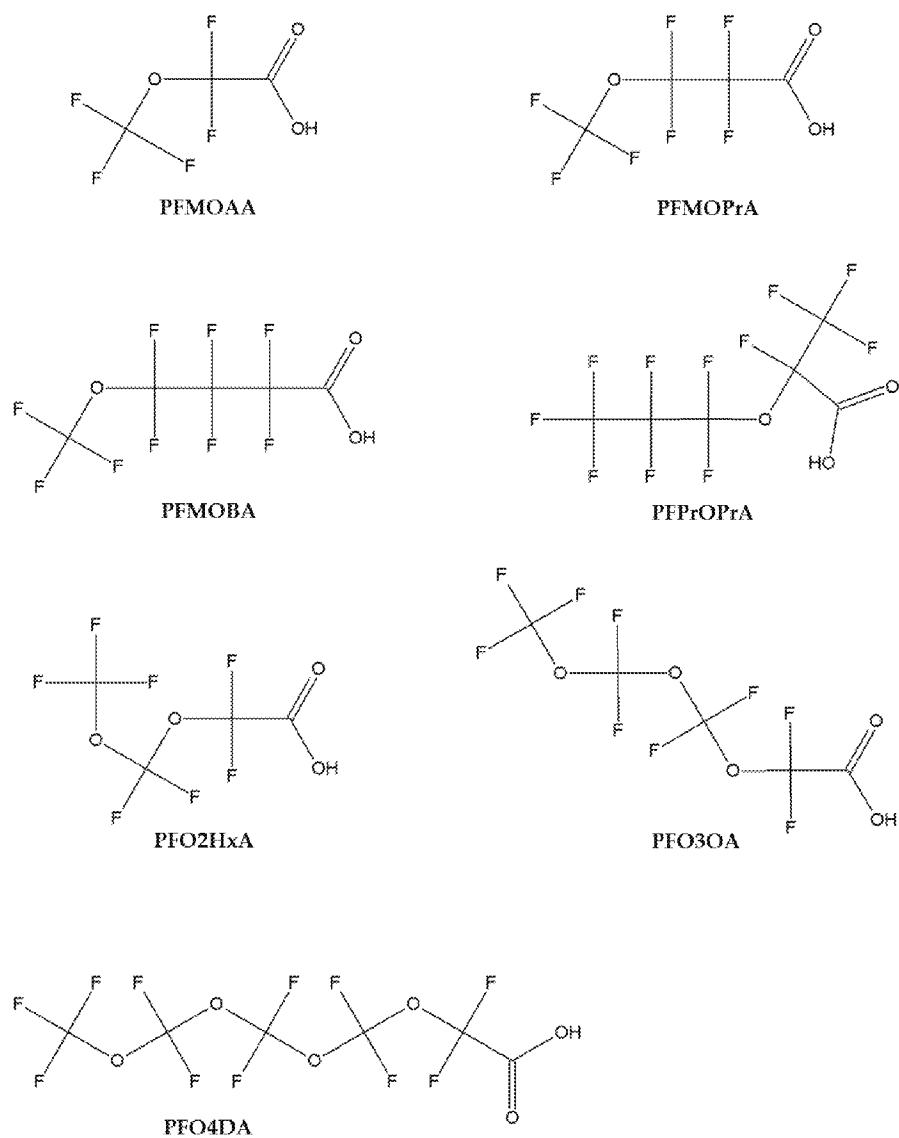
Table S6. Maximum, minimum, mean and median concentrations (ng/L) of PFASs in CFR watershed surface water as drinking water sources.\*

	Community A				Community B				Community C			
	max	min	median	mean	max	min	median	mean	max	min	median	mean
PFBA	99	<10	26	33	38	<10	12	12	104	<10	12	22
PFPeA	191	14	44	62	38	<10	19	19	116	<10	30	36
PFHxA	318	<10	48	78	42	<10	<10	11	24	<10	<10	<10
PFHpA	324	<10	39	67	85	<10	<10	11	24	<10	<10	<10
PFOA	137	<10	34	46	32	<10	<10	<10	17	<10	<10	<10
PFNA	38	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
PFDA	35	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
PFBS	80	<10	<10	<10	11	<10	<10	<10	<10	<10	<10	<10
PFHxS	193	<10	10	14	14	<10	<10	<10	14	<10	<10	<10
PFOS	346	<25	29	44	43	<25	<25	<25	40	<25	<25	<25
PFPrOPrA	<10	<10	<10	<10	10	<10	<10	<10	4560	55	304	631
PFOA+PFOS	447	0	64	90	59	0	0	9	55	<10	<10	<10
$\Sigma$ PFASs**	1502	18	212	355	189	0	47	62	4696	55	345	710

\* Concentrations < quantification limits were considered as zero to calculate means and  $\Sigma$  PFASs.

\*\* Other PFECAs were present in water samples from community C but could not be quantified and were therefore not included in  $\Sigma$  PFASs

Figure S1. Molecular structures of PEFCAs in this study



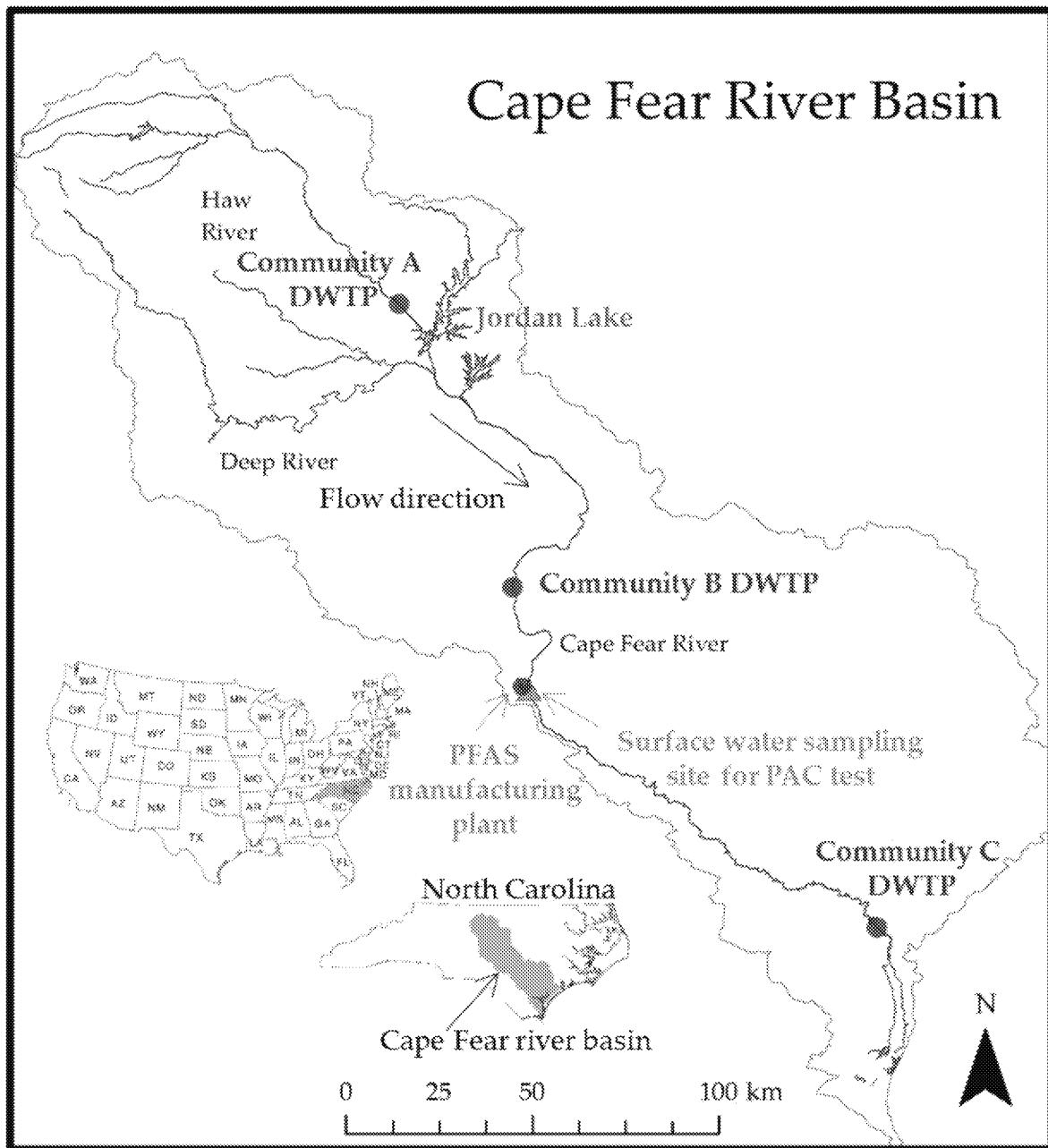
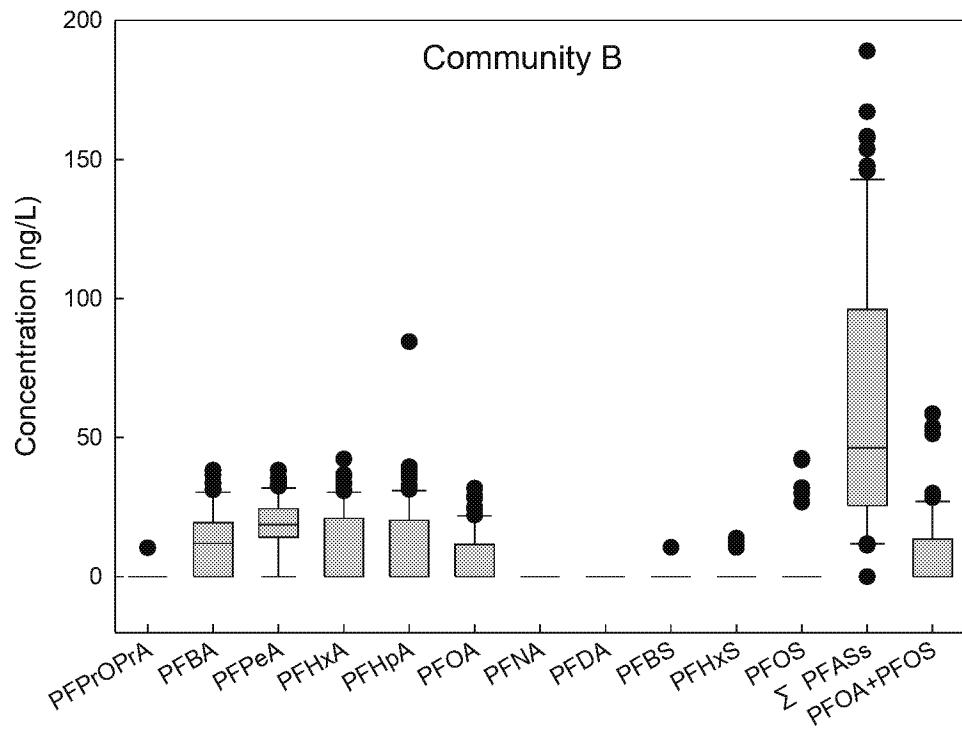
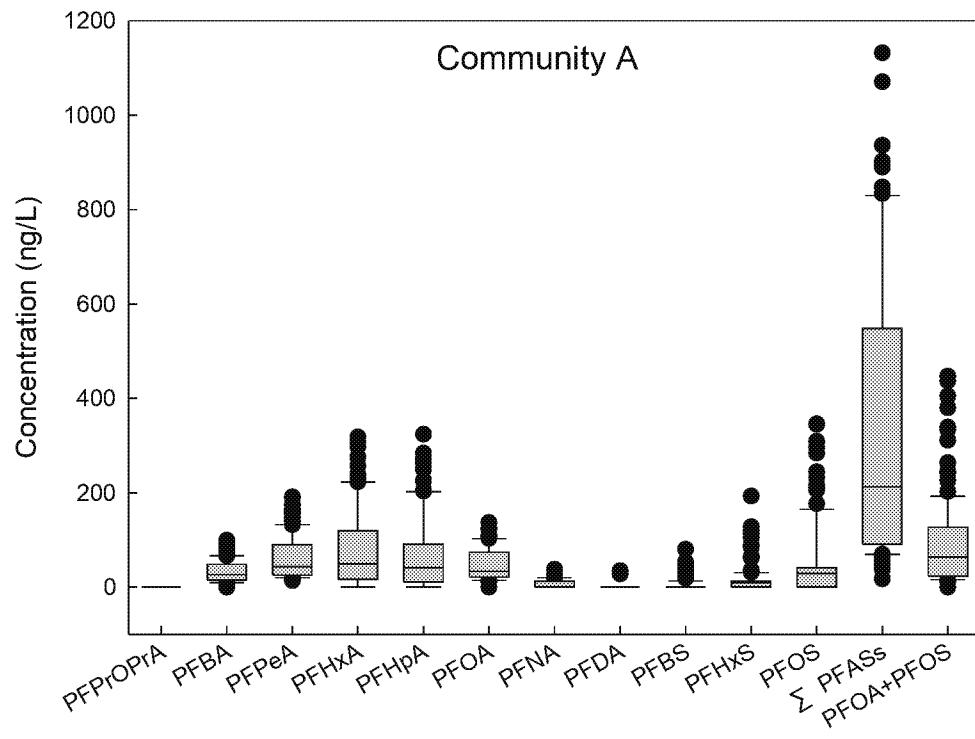


Figure S2. Sampling sites in the Cape Fear River watershed, North Carolina



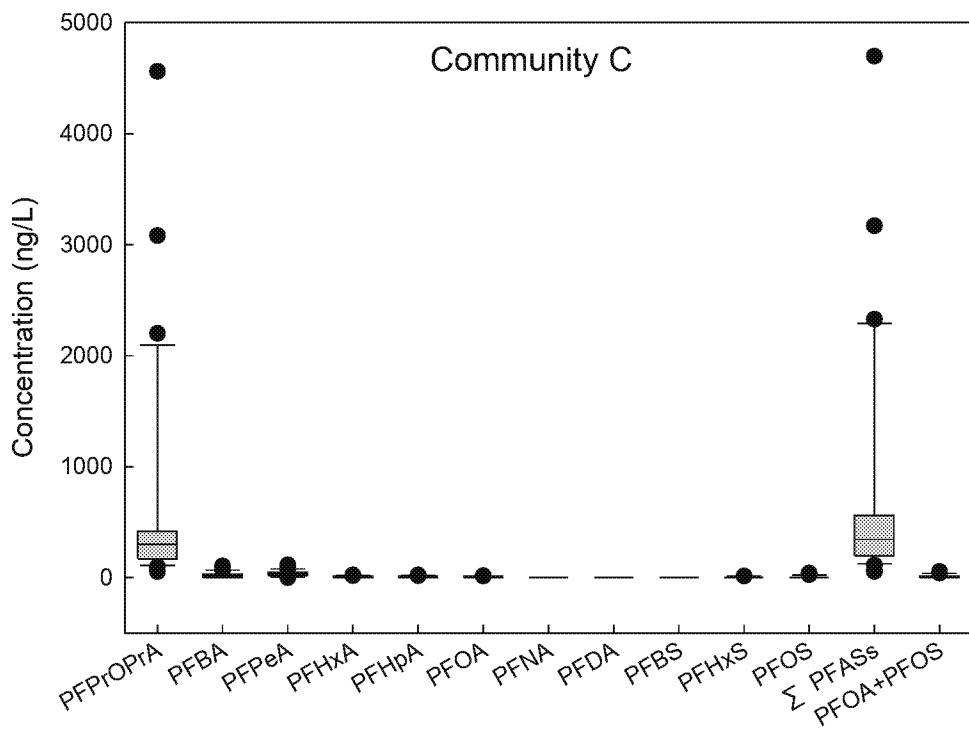


Figure S3. PFAS concentration distributions in the CFR watershed at three drinking water intakes. Concentrations < quantification limits were considered as zero. The upper and lower edges of a box represent the 75<sup>th</sup> and 25<sup>th</sup> percentile, respectively; the middle line represents the median; the upper and lower bars represent the 90<sup>th</sup> and 10<sup>th</sup> percentile, respectively; the dots represent outliers (>90<sup>th</sup> or <10<sup>th</sup> percentile).

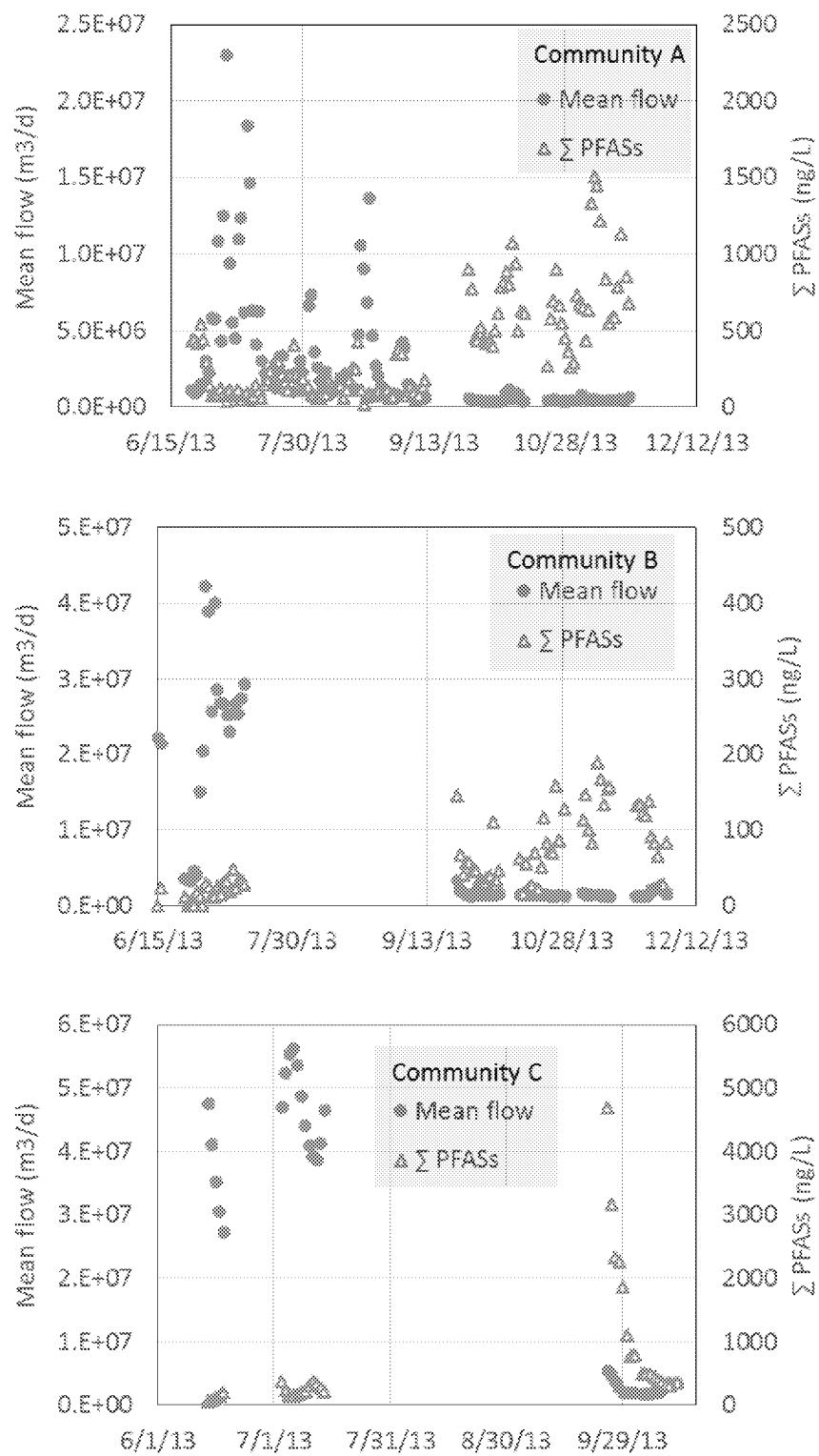


Figure S4. Total PFAS concentrations in the source water and stream flow at the three studied DWTPs. Stream flow data were acquired from US Geological Survey stream gage records

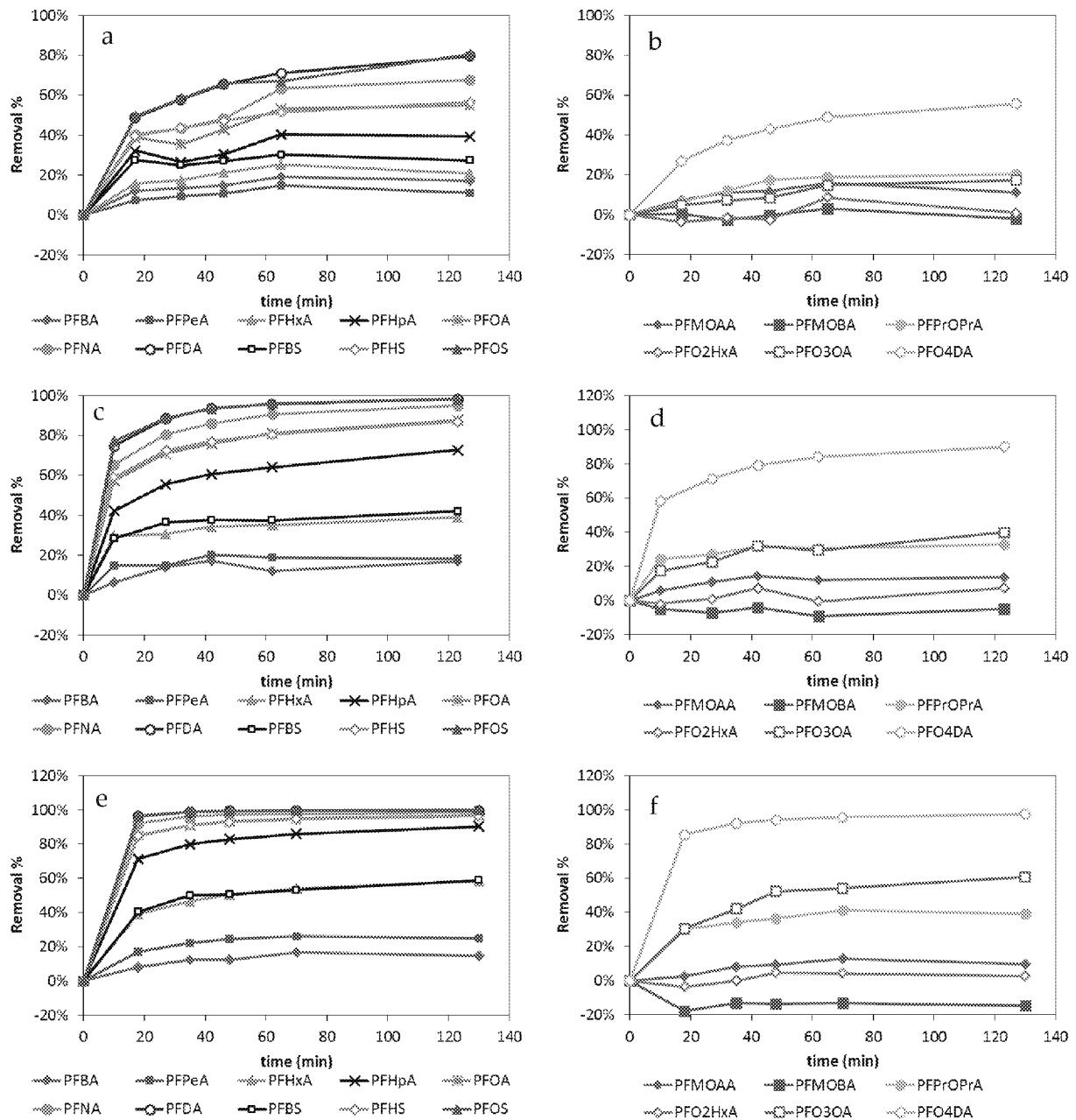


Figure S5. PFAS adsorption on PAC at carbon doses of (a, b) 30 mg/L, (c, d) 60 mg/L and (e, f) 100 mg/L. Figures show average PFAS removal percentages of duplicate tests.

## Reference

[ ADDIN EN.REFLIST ]